



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C09J 133/08, 7/02 // (C09J 133/08, 133:06)	A1	(11) International Publication Number: WO 94/20586 (43) International Publication Date: 15 September 1994 (15.09.94)
(21) International Application Number: PCT/US94/01872 (22) International Filing Date: 22 February 1994 (22.02.94) (30) Priority Data: 08/024,636 1 March 1993 (01.03.93) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventors: BAILEY, Dale, O.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). COOPRIDER, Terrence, E.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). DELGADO, Joaquin; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). MACNAMARA, Carol, E.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). MOST, Ronald, W.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). SAADAT, Shirin; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agents: SPRAGUE, Robert, W. et al.; Office of Intellectual Property Counsel, Minnesota Mining and Manufacturing Company, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

(54) Title: PRESSURE SENSITIVE ADHESIVE COMPRISING TACKY MICROSPHERES AND ACRYLAMIDE CONTAINING BINDER

(57) Abstract

The present invention comprises an adhesive composition containing a blend of microspheres and binder. The microspheres have at least one moiety containing a carboxylic acid group and the adhesive binder contains at least one acrylamide-based moiety. The binder is essentially free of pendant polymeric moiety with a T_g greater than 20 °C and a molecular weight in the range of about 2,000 to about 30,000.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

PRESSURE SENSITIVE ADHESIVE COMPRISING TACKY
MICROSPHERES AND ACRYLAMIDE CONTAINING BINDER

5 FIELD OF THE INVENTION

This invention relates to repositionable adhesives. In particular, it relates to a composition containing a blend of microspheres and a binder.

BACKGROUND OF THE INVENTION

10 Positionable adhesives are those which allow for the placement of an article containing such an adhesive onto a receptor in an exact position, because the article can be adjusted relative to the receptor after initial placement.

15 In some instances, the adhesive can be designated repositionable or repeatedly reusable. As used herein, the term "repositionable" refers to the ability to be repeatedly adhered to and removed from a substrate without substantial loss of adhesion
20 capability. Such adhesives exhibit aggressive tack but low peel adhesion properties, thus allowing repeated reusability. Commercial products such as the 3M Brand Post-It™ Notes display such adhesive characteristics.

Solid, inherently tacky, elastomeric
25 microspheres are known in the art to be useful in repositionable adhesive applications. Microsphere-based adhesives are thought to perform well in such applications at least in part due to their "self-cleaning" nature wherein substrate contaminants tend to
30 be pushed aside and trapped between the microspheres as the adhesive is applied. Upon removal, the adhesive still presents a relatively uncontaminated surface for reapplication to the substrat .

Such spheres having repositionable properties
35 are disclosed in U.S. Patent No. 3,691,140 (Silver). These microspheres are prepared by aqueous suspension

- 2 -

polymerization of alkyl acrylate monomers and ionic comonomers, e.g., sodium methacrylate, in the presence of an emulsifier, preferably an anionic emulsifier.

U.S. Patent No. 4,166,152, (Baker et al.)

5 describes solid, inherently tacky (meth)acrylate microspheres which are prepared from non-ionic alkyl acrylate or methacrylate monomer(s) in the presence of both an emulsifier and an ionic suspension stabilizer having an interfacial tension sufficient to prevent
10 microsphere agglomeration. Such microspheres are also described in U.S. Patent No. 4,495,318 and 4,598,112 (Howard), where the preparative methods involve the use of a nonionic emulsifier or cationic emulsifier.

U.S. Patent No. 4,786,696, (Bohnel) describes
15 a suspension polymerization process for preparing solid, inherently tacky (meth)acrylate microspheres which do not require the use of either an ionic comonomer or an ionic suspension stabilizer in order to prevent agglomeration. The process requires agitation
20 of the vessel charge prior to the initiation of the reaction sufficient to create a suspension of monomer droplets having an average monomer droplet size of between about 5 to about 70 micrometers. In addition to the (meth)acrylate monomer, a minor portion of a
25 vinylic comonomer such as, e.g., acrylic acid, may be included to modify the "tacky nature" of the microspheres.

DE 3,544,882 A1, (Nichiban) describes crosslinked microspheres which can be composed of a
30 (meth)acrylate ester and a vinyl monomer, e.g., acrylic acid. The microspheres have a reactive functional group through which crosslinking is achieved. When tacky, the spheres are said to be useful as "removable adhesives." The microspheres can contain other
35 monomers to prevent partial transfer of the adhesive when a backing is pulled away from the substrate. Useful monomers include vinyl acetate, styrene and

- 3 -

acrylonitrile. These additional monomers may be present in amounts up to 50 percent of the (meth)acrylate ester monomer.

U.S. Patent No. 5,045,569 (Delgado) describes
5 hollow, inherently tacky (meth)acrylate microspheres which can be prepared from alkyl acrylate or methacrylate monomer(s) in the presence of polar monomers such as acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid and fumaric
10 acid.

One problem associated with these types of adhesives has been microsphere transfer, i.e., microsphere loss to the substrate. To alleviate this problem, binders or primers have been utilized.

15 For example, U.S. Patent No. 3,857,731 (Merrill et al.) teaches the use of binders. Merrill et al. coats sheet materials with the tacky elastomeric copolymer microspheres described in Silver and a binder material which provides sockets in which microspheres
20 are predominantly held by mechanical forces. Additional chemical forces are not needed; indeed, Merrill et al. states in column 1, at line 62, that the binder "need not have a high degree of adhesion for the microspheres, and in fact, binders having an extremely
25 low adhesion for the microspheres provide an excellent microsphere retaining surface." A wide range of useful binders are disclosed including hard resins such as epoxy or nitrocellulose composition, soft resins such as a vinyl ether, urethanes, fluorochemicals, silicones
30 and microcrystalline waxes. Especially preferred soft resins include the acrylate/acid copolymers described in U.S. Reissue Patent No. 24,906 (Ulrich).

Another approach for reducing microsphere loss is disclosed in EPO 209,337 (Thomson et al.).
35 Thomson et al. teach that microsphere adhesives may contain an adhesion promoting monomer, such as vinyl pyridine having a functionality which is unreacted

- 4 -

during polymerization, and is, therefore, available for subsequent binding to the substrate, which may be primed. Alternatively, the adhesion promoting monomer can be a carboxyl group which can be linked to an ionizing agent in the substrate and/or binder. It is disclosed that the binder may be blended with the microspheres.

Another attempt to limit microsphere transfer is disclosed in U.S. Patent No. 4,735,837 (Miyasaka et al.) which teaches the use of a detachable adhesive sheet having an adhesive layer containing "elastic micro-balls" and an adhesive. The elastic microballs, which may or may not be tacky, can be derived by suspension polymerizing a (meth)acrylate monomer and an α -olefinic carboxylic acid monomer in an aqueous medium. In addition to the microballs, the detachable adhesive sheet includes adhesives such as polyacrylic ester copolymers, polyisobutylene-series adhesives, styrene-ethylene-butylene-styrene block copolymers series adhesives. The micro-balls and an adhesive are dispersed in solvent, mixed and coated, with the ratio of adhesive to micro-balls being 1:10 to about 10:1 so that all of the micro-balls are completely covered with adhesive.

U.S. Patent No. 4,656,218 (Kinoshita) also discloses a releasable sheet. Kinoshita coats a releasable sheet with a microsphere adhesive prepared by suspension polymerization followed by emulsion polymerization wherein a latex binder is formed in situ from alpha-olefin carboxylic acids such as acrylic acid. The latex is disclosed to consist of microparticles having an average diameter from about 1 to about 4 microns. Tackifiers are disclosed as preferred optional ingredients.

Another attempt to overcome this difficulty associated with microsphere transfer is described in U.S. Patent No. 4,822,670. (Ono et al.). Ono et al.

- 5 -

teach the use of a removable adhesive sheet or tape comprised of adhesive fine particles attached on at least one side of a substrate through a primer resin layer. The primer resin layer can comprise

5 poly(vinylidene chloride) resins, poly(vinyl acetate) resins, polyamide resins, poly(vinyl chloride-acetate) type resins, phenol-modified epoxy resins and maleated natural rubbers. The adhesive fine particles disclosed are copolymers comprising a (meth)acrylic ester which

10 may include a functional group such as a carboxylic group.

U.S. Patent No. 4,994,322 (Delgado et al.) discloses another way of reducing microsphere transfer. Delgado et al. teaches the use of a pressure-sensitive

15 adhesive comprising a binder copolymer and hollow, elastomeric microspheres. The hollow microspheres include at least one alkyl acrylate or alkyl methacrylate ester which can be copolymerized with monomers such as acrylic acid, methacrylic acid,

20 itaconic acid, crotonic acid, maleic acid and fumaric acid. The Delgado et al. adhesive comprises a binder copolymer which includes a polymeric backbone containing repeating A and C monomers and from about 1% to about 20% B monomers. A is a monomeric acrylic or

25 methacrylic acid ester. B is a polar monomer which can be a mono-olefinic, mono- and dicarboxylic acid or salt thereof. B can also be an acrylamide, acrylonitrile and methacrylonitrile. C is a monomer having the general formula $X-(Y)_n-Z$ wherein X is a vinyl group

30 copolymerizable with the A and B monomers, Y is a divalent linking group and Z is a monovalent polymeric moiety having a T_g greater than 20°C and a molecular weight in the range of about 2,000 to about 30,000. The binder copolymer has a shear storage modulus of at

35 least 1×10^5 Pascals at 3 Hz and 22°C.

- 6 -

Another attempt to limit microsphere transfer is described in U.S. Patent No. 5,128,412. (Miyasaka). Miyasaka teaches the use of a removable adhesive composition wherein elastic microballs are crosslinked to an adhesive copolymer. The microballs comprise an acrylate or methacrylate acid ester which can have at least one carboxyl group. The adhesive copolymer includes an acrylate or methacrylate monomer copolymerized with at least one of the following groups: (1) a carboxyl group, (2) a hydroxyl group, (3) an amino group, i.e., acryl amide and (4) an epoxy group. The two, i.e., the microballs and the adhesive copolymer, are crosslinked by crosslinking agents such as polyepoxies, polyisocyanates and polyfunctional aziridines.

It has now been found that microsphere transfer can be reduced in an adhesive blend comprising microspheres and adhesive binder by utilizing carboxylated microspheres and a binder incorporating at least one acrylamide-based moiety. Unexpectedly, it has been found that there is no need to utilize a crosslinking agent with the adhesive blend.

SUMMARY OF THE INVENTION

The present invention comprises a blend of microspheres and an adhesive binder wherein the microspheres are not crosslinked by a crosslinking agent to the adhesive binder. The microspheres which are inherently tacky and elastomeric have at least one moiety containing at least one carboxylic acid group. The adhesive binder comprises a sufficient amount of at least one acrylamide-based moiety to substantially reduce microsphere transfer.

In one embodiment of the present invention, the composition is an aqueous blend of the microspheres and the adhesive binder.

In another embodiment of the present invention, the composition is an organic dispersion

- 7 -

comprising an organic liquid, the microspheres and the binder.

In a preferred embodiment of the present invention, the binder further comprises at least one
5 acrylic acid ester and/or methacrylic acid ester copolymerized with an acrylamide.

The following terms have these meanings as used herein:

- 10 1. The term "droplet" means the liquid stage of the microspheres prior to the completion of polymerization.
- 15 2. The term "cavity" means a space within the walls of a droplet or microsphere when still in the suspension or dispersion medium prior to drying, and thus containing whatever medium was used.
- 20 3. The term "void" means empty space completely within the walls of a polymerized microsphere.

All weights, parts and ratios herein are by weight unless specifically stated otherwise.

DETAILED DESCRIPTION OF THE INVENTION

The present invention involves an adhesive
25 composition which has low microsphere transfer. The composition comprises a blend of polymeric microspheres and an adhesive binder.

The microspheres utilized in the present invention can be either hollow or solid. If the
30 microspheres are hollow, they should comprise at least one alkyl acrylate or alkyl methacrylate ester and at least one moiety containing a carboxylic acid group.

Alkyl acrylate or methacrylate monomers useful in preparing the hollow microspheres for
35 pressure-sensitive adhesives of this invention are those monofunctional unsaturated acrylate or methacrylate esters of non-tertiary alkyl alcohols, the

- 8 -

alkyl groups of which have from 4 to 14 carbon atoms. Such acrylates are oleophilic, water emulsifiable, have restricted water solubility and as homopolymers, generally have a glass transition temperature below about -20°C. Included within this class of monomers are, for example, isooctyl acrylate, 4-methyl-2-pentyl acrylate, 2-methylbutyl acrylate, isoamyl acrylate, sec-butyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, isodecyl methacrylate, isononyl acrylate, isodecyl acrylate and the like, singly or in mixtures.

Preferred acrylates include isooctyl acrylate, isononyl acrylate, isoamyl acrylate, isodecyl acrylate, 2-ethylhexyl acrylate, n-butyl acrylate, sec-butyl acrylate and mixtures thereof. Acrylate or methacrylate or other vinyl monomers which, as homopolymers, have glass transition temperatures higher than about -20°C, e.g., tert-butyl acrylate, isobornyl acrylate, butyl methacrylate, vinyl acetate, N-vinyl pyrrolidone, acrylamide and the like may be utilized in conjunction with one or more of the acrylate or methacrylate monomers provided that the glass transition temperature of the resultant polymer is below about -20°C.

Monomers having carboxylic functionality include, but are not limited, to mono-, di-, and polycarboxylic acids, salts and mixtures thereof. Preferred monomers include acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid and fumaric acid.

The hollow microspheres of this invention comprise at least 85 parts by weight of at least one alkyl acrylate or alkyl methacrylate ester and corresponding, up to about 15 parts by weight of one or more monomers having a carboxylic functionality. Preferably, the monomers having carboxylic functionality comprise up to 10 parts by weight of the

- 9 -

hollow microsphere. More preferably, the monomers comprise from 2 to about 6 parts by weight microsphere.

The microspheres of the present invention are prepared by aqueous suspension polymerization.

- 5 Suspension polymerization is a procedure whereby a monomer is dispersed in a medium usually aqueous in which it is insoluble and the polymerization allowed to proceed within the individual monomer droplets. The kinetics and mechanism are essentially those for the
- 10 corresponding bulk polymerization under the same conditions and initiator concentration.

Aqueous suspensions of the hollow microspheres may be prepared by a "two-step" emulsification process which first involves forming a

15 water-in-oil emulsion of an aqueous solution of the carboxylic monomer in oil phase monomer, i.e., at least one acrylate or methacrylate ester, using an emulsifier having a low hydrophilic-lipophilic balance (HLB) value. Suitable emulsifiers are those having an HLB

20 value below about 7, preferably in the range of about 2 to about 7. Examples of such emulsifiers include sorbitan mono-oleate, sorbitan trioleate and ethoxylated oleyl alcohol such as Brij™ 93 available from Atlas Chemical Industries, Inc. Thus, in this first step, oil

25 phase monomer(s), emulsifier, a free radical initiator and optionally, a crosslinking monomer or monomers as defined below are combined, and an aqueous solution of all or a portion of the carboxylated monomer(s) is agitated and poured into the oil phase mixture to form

30 a water-in-oil emulsion. A thickening agent, e.g., methyl cellulose, may also be added to the aqueous phase of the water-in-oil emulsion. In the second step, a water-in-oil-in-water emulsion is formed by dispersing the water-in-oil emulsion of the first step

35 into an aqueous phase containing an emulsifier having an HLB value above about 6. The aqueous phase may also contain a portion of the carboxylated monomer(s) which

- 10 -

was not added in step one. Examples of such emulsifiers include ethoxylated sorbitan mono-oleate, ethoxylated lauryl alcohol and alkyl sulfates. In both steps, when an emulsifier is added, its concentration should be greater than its critical micelle concentration, which is herein defined as the minimum concentration of emulsifier necessary for the formation of micelles, i.e., submicroscopic aggregations of emulsifier molecules. Critical micelle concentration is slightly different for each emulsifier, usable concentrations ranging from about 1.0×10^{-4} to about 3.0 moles/liter. Additional detail concerning the preparation of water-in-oil emulsions, i.e., multiple emulsions may be found in various literature references, e.g., Surfactant Systems: Their Chemistry, Pharmacy & Biology, (D. Attwood and A.T. Florence, Chapman & Hall Limited, New York, N.Y., 1983). Next, initiators are added. Useful initiators are those which are normally suitable for free radical polymerization of acrylate monomers. Examples of such initiators include thermally-activated initiators such as azo compounds, hydroperoxides, peroxides and the like and photoinitiators such as benzophenone, benzoin ethyl ether and 2,2,-dimethoxy-2 phenyl acetophenone. The initiator is generally used in amounts ranging from 0.01 percent up to about 10 percent by weight of the total polymerizable composition, preferably up to about 5 percent. Upon addition, heat or radiation are applied to initiate polymerization of the monomers which is an exothermic reaction.

Aqueous suspensions of the hollow microspheres may also be prepared by a "one-step" emulsification process comprising aqueous polymerization of at least one alkyl acrylate or alkyl methacrylate ester monomer and one monomer having a carboxylic functionality in the presence of at least one emulsifier capable of producing a water-in-oil

- 11 -

emulsion inside the droplets which is substantially stable during emulsification and polymerization. In general, emulsifiers having a high HLB value are desired, i.e., a value of at least about 25. Examples of such emulsifiers include alkylarylether sulfates such as sodium alkylarylether sulfate, e.g., Triton™ W/30 commercially available from Rohm and Haas, alkylarylpolyether sulfates such as alkylarylpoly(ethylen oxide) sulfates alkyl sulfates such as sodium lauryl sulfate, ammonium lauryl sulfate, triethanolamine lauryl sulfate and sodium hexadecyl sulfate. Alkyl sulfates, alkyl ether sulfates and alkylarylether sulfates are preferred as they provide a maximum void volume per microsphere for a minimum amount of surfactant. Polymeric stabilizers may also be present, but are not necessary.

The microsphere composition may also contain a crosslinking agent. Examples of useful crosslinking agents include, but are not limited to: multifunctional (meth)acrylate(s), e.g., butanediol diacrylate or hexanediol diacrylate or other multifunctional crosslinkers such as divinylbenzene and mixtures thereof. When used, crosslinker(s) is (are) added at a level of up to about 0.15 equivalent weight percent, preferably up to about 0.1 equivalent weight percent, of the total polymerizable composition. The "equivalent weight percent" of a given compound is defined as the number of equivalents of that compound divided by the number of equivalents in the total composition wherein the equivalent is the number of grams divided by the equivalent weight. The equivalent weight means the molecular weight divided by the number of polymerizable groups in the monomer (in the case of those monomers with only one polymerizable group, equivalent weight = molecular weight).

The hollow microspheres are normally tacky, elastomeric, insoluble, but swellable, in organic

- 12 -

solvents and small, typically having diameters of at least 1 micrometer to about 250 micrometers. The voids typically range in size up to about 100 micrometers or larger. The majority of the hollow microspheres

5 prepared by the methods of this invention contain at least one void with a void diameter which is at least about 10% of the diameter of the microsphere, preferably at least about 20%, more preferably, at least about 30%.

10 Following polymerization, an aqueous suspension of the hollow microspheres is obtained which is stable to agglomeration or coagulation under room temperature conditions. The suspension may have non-volatile solids contents of from about 10 to about 50
15 percent by weight. Upon prolonged standing, the suspension separates into two phases, one phase being aqueous and substantially free of polymer, the other phase being an aqueous suspension of microspheres having at least one cavity which, upon drying, becomes
20 a void. Decantation of the microsphere-rich phase provides an aqueous suspension having a non-volatile solids content on the order of about 40-50 percent, which, if shaken with water, will redisperse.

If desired, the aqueous suspension may be
25 coagulated with polar organic solvents such as methanol, with ionic emulsifiers having a charge opposite to that of the emulsifier used in the polymerization process, or with saturated salt solutions, or the like, followed by washing and drying.
30 The partially dried microspheres with sufficient agitation will readily redisperse in common organic liquids such as ethyl acetate, tetrahydrofuran, heptane, 2-butanone, benzene, cyclohexane and esters although it is not possible to resuspend them in water.

35 Alternatively, solid microspheres may be used. If solid microspheres are used, they should comprise at least one alkyl acrylate or alkyl

- 13 -

methacrylate ester and a monomer having at least one moiety containing a carboxylic acid functionality.

Alkyl acrylate or methacrylate monomers useful in preparing the solid microspheres for
5 pressure-sensitive adhesives of this invention are those monofunctional unsaturated acrylate or methacrylate esters of non-tertiary alkyl alcohols, the alkyl groups of which have from 4 to 14 carbon atoms. Such acrylates are oleophilic, water emulsifiable, have
10 restricted water solubility and as homopolymers, generally have a glass transition temperature below about -20°C. Included within this class of monomers are, for example, isooctyl acrylate, 4-methyl-2-pentyl acrylate, 2-methylbutyl acrylate, isoamyl acrylate,
15 sec-butyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, isodecyl methacrylate, isononyl acrylate, isodecyl acrylate and the like, singly or in mixtures.

Preferred acrylates include isooctyl acrylate, isononyl acrylate, isoamyl acrylate, isodecyl
20 acrylate, 2-ethylhexyl acrylate, n-butyl acrylate, sec-butyl acrylate and mixtures thereof. Acrylate or methacrylate or other vinyl monomers which, as homopolymers, have glass transition temperatures higher than about -20°C, e.g., tert-butyl acrylate, isobornyl
25 acrylate, butyl methacrylate, vinyl acetate, N-vinyl pyrrolidone, acrylamide and the like may be utilized in conjunction with one or more of the acrylate or methacrylate monomers provided that the glass transition temperature of the resultant polymer is
30 below about -20°C.

Monomers having carboxylic functionality include, but are not limited, mono-, di- and polycarboxylic acids, salts and mixtures thereof. Examples of such acids include acrylic acid,
35 methacrylic acid, itaconic acid, crotonic acid, maleic acid, and fumaric acid.

- 14 -

Solid microspheres can be prepared by an aqueous suspension polymerization technique utilizing emulsifiers in an amount greater than the critical micelle concentration. Critical micelle concentration is defined as that minimum emulsifier concentration necessary for the formation of micelles. The critical micelle concentration is slightly different for each emulsifier. Useable concentrations typically range from about 1.0×10^{-4} to about 3.0 moles per liter.

5 Anionic, nonionic or cationic emulsifiers can be used. Typical examples of anionic emulsifiers include sodium dodecylbenzene sulfonate, sodium salts of alkyl aryl ether sulfonates and the like. Examples of nonionic emulsifiers include ethoxylated oleyl alcohol and

15 polyoxyethylene octylphenyl ether and a useful cationic surfactant is a mixture of alkyl dimethylbenzyl ammonium chlorides wherein the alkyl chain is from ten to eighteen carbons long. While only examples of anionic, nonionic and cationic emulsifiers are given

20 herein, it is believed that amphoteric emulsifiers would likewise work.

Initiators effecting polymerization are those which are normally suitable for free-radical polymerization of acrylate monomers. Examples of such

25 initiators include thermally-activated initiators such as azo compounds, hydroperoxides, peroxides and the like and photoinitiators such as benzophenone, benzoin ethyl ether and 2,2,-dimethoxy-2-phenyl acetophone. Other suitable initiators include lauryl peroxide and

30 bis(t-t-butyl cyclohexyl)peroxy dicarbonate. The initiator concentration should be sufficient to bring about a complete monomer conversion in a desired time span and temperature range. Parameters which affect the concentration of initiator employed include the

35 type of initiator and particular monomer and/or monomers involved. It is believed that effective concentrations range from about 0.10 to about 1 percent

- 15 -

by weight of the total monomers and more preferably, from about 0.25 to about 0.70 percent by weight monomers and/or monomers. Polymeric stabilizers may also be present, but are not necessary. Upon addition, 5 heat or radiation are applied to initiate the polymerization of the monomers which is an exothermic reaction.

The solid microsphere composition may also contain a crosslinking agent. Examples of useful 10 crosslinking agents include, but are not limited to: multifunctional (meth)acrylate(s), e.g., butanediol diacrylate or hexanediol diacrylate or other multifunctional crosslinkers such as divinylbenzene and mixtures thereof. When used, crosslinker(s) is (are) 15 added at a level of up to about 0.15 equivalent weight percent, preferably up to about 0.1 equivalent weight percent, of the total polymerizable composition. The "equivalent weight percent" of a given compound is defined as the number of equivalents of that compound 20 divided by the number of equivalents in the total composition, wherein the equivalent is the number of grams divided by the equivalent weight.

Following polymerization, a stable aqueous suspension of solid microspheres at room temperature is 25 obtained. The suspension may have non-volatile solids contents of from about 10 to about 50 percent by weight. Upon prolonged standing, the suspension separates into two phases, one being aqueous and in essence free of polymer and the other being an aqueous 30 suspension of the polymeric sphere. The aqueous suspension of microspheres may be utilized immediately following polymerization, because the suspension is stable to agglomeration or coagulation, under room temperature conditions. Decantation of the 35 microsphere-rich phase provides an aqueous suspension having a non-volatile solids content, which if shaken, will readily redisperse.

- 16 -

Alternatively, the suspension may be coagulated with an organic liquid such as methanol, followed by washing and drying. These partially dried polymer spheres, with sufficient agitation, will
5 readily suspend in a variety of common organic solvents such as ethyl acetate, tetrahydrofuran, heptane, 2-butanone, benzene cyclohexane and esters.

Suitable binders include polyacrylamides. The acrylamides which can be used in the present
10 invention are the reaction products of an acrylic or methacrylic acid with ammonia or primary or secondary amines. Examples of suitable acrylamides include, but are not limited to, acrylamide, isooctyl acrylamide, 2-ethyl hexyl acrylamide, and N,N-dimethyl acrylamide.

15 If desired, the acrylamides can be copolymerized with one or more monomers having vinyl groups. Any vinyl monomer may be used so long as the product acts as a binder for the microspheres. Suitable monomers include alkyl acrylates or
20 methacrylates. Alkyl acrylate or methacrylate monomers useful in preparing the binder are those monofunctional unsaturated acrylate or methacrylate esters of non-tertiary alkyl alcohols, the alkyl groups of which have from 4 to 14 carbon atoms. Examples of such
25 monomers include esters of acrylic acid or methacrylic acid with non-tertiary alkyl alcohols such as 1-butanol, 1-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, 2-ethyl-1-butanol, 3,5,5-trimethyl-
30 1-hexanol, 3-heptanol, 2-octanol, 1-decanol, 1-dodecanol, isooctyl alcohol, isononyl alcohol, 2-ethyl-hexyl alcohol and the like. Such monomeric acrylic or methacrylic esters are known in the art and many are commercially available.

35 Preferably, the binder comprises up to about 15 parts acrylamide and from about 85 to about 100 parts by weight acrylic or methacrylic ester. More

- 17 -

preferably, the binder comprises from about 4 to about 10 parts acrylamide and from about 91 to about 96 parts acrylic or methacrylic ester. It is also preferred for optimum results that the binder have an inherent
5 viscosity ("I.V.") of at least 0.2 dl/g although lower I.V.'s can be used depending upon user preference. Most preferably, the binder should have an I.V. of least 0.6 dl./g.

The adhesive of this invention is made by
10 combining the binder with the microspheres. If an organic dispersion of the adhesive is desired, a solution of binder is combined with an organic dispersion of microspheres. If an aqueous adhesive composition is desired, an aqueous suspension of
15 microspheres is combined with an aqueous solution of binder. Preferably, the weight of the binder comprises from about 1 to about 40 parts by weight of the adhesive and the microspheres comprise from about 60 to about 99 parts by weight of adhesive of this invention.

20 Properties of the pressure-sensitive adhesives of the present invention can be altered by the addition of a tackifying resin(s) and/or plasticizer(s). Preferred tackifiers for use herein include hydrogenated rosin esters commercially
25 available from such companies as Hercules, Inc. under the tradenames Foral™ and Pentalyn™. Individual tackifiers include those based on t-butyl styrene. Useful plasticizers include dioctyl phthalate, 2-ethyl hexyl phosphate, tricresyl phosphate and the like.

30 Optionally, colorants, fillers, stabilizers and various other polymeric additives can be utilized.

Suitable backing materials for the adhesive composition include, but are not limited to, paper, plastic films, cellulose acetate, ethyl cellulose,
35 woven or nonwoven fabric formed of synthetic or natural materials, metal, metallized polymeric film, ceramic sheet material and the like.

- 18 -

The following examples are illustrative in nature and are not intended to limit the invention in any way.

TEST METHODS

5

PEEL ADHESION

Peel adhesion is the force required to remove a polyester film applied to the coated test material measured at a specific angle and rate of removal. In the examples, this force is expressed in grams per 1.25
10 inch width of coated sheet. The procedure followed is:

A strip, 1.25 inches wide, of polyester film is applied to the horizontal surface of a coated sample fixed on a test plate. A 4.5 lb. hard rubber roller is used to apply the strip. The free end of the polyester
15 film is attached to the adhesion tester load cell so that the angle of removal will be 90 degrees. The test plate is then clamped in the jaws of the tensile testing machine which is capable of moving the plate away from the load cell at a constant rate of 12 inches
20 per minute. A load cell reading in grams per 1.25 inches of coated strip is recorded as the polyester film is peeled from the coated samples. The samples are tested three times. The average of the three tests is reported below.

25

MICROSPHERE TRANSFER

Microsphere transfer for the purposes of this test is defined as the amount of microsphere that transfers to an applied paper when the coated sample is removed from the paper. It is measured as the percent
30 of the area covered with microspheres. The procedure followed is:

A three-quarter (3/4") wide strip of microsphere coated sample is adhered to a clean area of a clay coated paper commercially available as Kromcoat,
35 for a few seconds using the mechanical rolling action provided by an TLMI release and adhesion tester and then is removed at a 90° degree angle at a constant

- 19 -

rate. The clay coated strip is then surveyed by an image processor through a video camera and the percent microsphere coverage of the viewed area is recorded. Ten fields are surveyed on the test sample and the
5 average of these readings is recorded.

ABBREVIATIONS

AA - acrylic acid
ACM - acrylamide
CRA - crotonic acid
10 FA - fumaric acid
IOA - isooctyl acrylate
IPA - isopropyl alcohol
ITA - itaconic acid

15

EXAMPLESEXAMPLE 1

Example 1 which illustrates the use of a solvent base Isooctyl acrylate/acrylamide copolymer binder with hollow isooctyl acrylate/acrylic acid
20 microspheres was prepared in the following manner:

A one liter 3-necked flask equipped with a thermometer, a reflux condenser, a mechanical stirrer, and a gas inlet tube was charged with 739 grams of deionized water, 239 grams of isooctyl acrylate, 6.12
25 grams of acrylic acid 0.8 grams of Lucidol 70 (a 70 percent active benzoyl peroxide, commercially available from Pennwalt Corporation) and 10 grams of 28.5 percent by weight active ammonium lauryl sulfate sold as Standapol A by the Henkel Corp. The agitation was set
30 at 600 revolutions per minute (rpm), and the reaction mixture was purged with nitrogen. The stirring and nitrogen purges were maintained throughout the reaction period. The reaction mixture was allowed to stir at room temperature for 15 minutes and then was heated to
35 70° C to initiate the reaction. The reaction became exothermic after 30 minutes of heating. After the

- 20 -

exotherm had subsided the batch was heated to 75° C for 4 hours.

Thereafter, the reaction mixture was cooled to room temperature and filtered through a cheese cloth. The resulting suspension was found to contain hollow microspheres with a mean diameter of 40 microns. The microspheres were allowed to separate, coagulated with IPA and then re-dispersed in heptane to yield a 8% solids dispersion of copolymer microspheres in solvent.

10 The copolymer binder was prepared in a glass reaction bottle by combining 300 grams of ethyl acetate, 0.6 grams of VAZO-64, 16 grams of acrylamide, 0.08 grams of carbon tetrabromide and 184 grams of isooctyl acrylate. The bottle was then purged with Argon, sealed and tumbled in a water bath at 55°C for 24 hours.

The copolymer binder was then mixed with the copolymer microspheres at a 93/7 (microsphere/binder) weight ratio at 9% solids. The dispersion was then coated on plain bond paper at 0.45 gm/sq.ft. dry weight. The acrylate/acrylamide ratio of the binder, the weight percent of the binder in the dispersion and the test results are reported in Table 1.

COMPARATIVE EXAMPLE 1

25 Comparative Example 1 discloses the use of hollow isooctyl acrylate/acrylic acid copolymer microspheres alone with no binder present. The adhesive of Comparative Example 1 was prepared in the following manner:

30 The microspheres were made in accordance with the procedure outlined in Example 1. Once made, the microspheres were dispersed in heptane at 9% solids. Thereafter, the microspheres were coated onto plain bond paper at 0.45 gm/sq.ft. dry weight and tested. 35 The test results are described in Table 1 below.

- 21 -

EXAMPLES 2-8

Examples 2-8 illustrate the use of an adhesive blend comprising a solvent-based acrylamide copolymer binder and an acrylic acid/isooctyl acrylate copolymer microsphere. The blends of these examples were prepared in accordance with the procedures outlined in Example 1. Binders with different amounts of acrylamide were prepared by changing the isooctyl acrylate/acrylamide ratio in the recipe. The acrylate/acrylamide ratio of the binder, the weight percent of the binder and the test results are reported in Table 1.

TABLE 1

Example #	Binder IOA/ACM Ratio	% by Wt. Binder	Peel Adhesion (gm/1.25")	Micro- sphere Transfer (%)
1	98/2	7	78	13.8
2	98/2	3	73	15.8
3	98/2	5	67	11.7
4	98/2	1	74	15.0
5	90/10	1	90	3.0
6	90/10	3	80	1.5
7	90/10	5	94	.3
8	90/10	7	92	.4
C1	0	0	73	27.0

The test results indicate that the adhesive blend of the present invention effectively reduces microsphere even at low concentrations of binder.

EXAMPLE 9

Example 9 illustrates the use of an adhesive blend comprising a water-based acrylamide binder and solid isooctyl/acrylic acid microspheres. The adhesive was prepared in the following manner:

- 22 -

A one liter 3-necked flask equipped with a thermometer, a reflux condenser, a mechanical stirrer and a gas inlet tube was charged with 739 grams of deionized water, 239 grams of isooctyl acrylate, 14.7 grams of acrylic acid, 0.8 gram Lucidol 70 and 10 grams of sodium alkyl aryl polyether sulfonate commercially available as Triton X 200 from the Rohm and Haas Company of Philadelphia, Pennsylvania. The mixture was then stirred by an agitator at a rate of 600 revolutions per minute and was purged with nitrogen. The stirring and the nitrogen purge was maintained throughout the reaction period. The reaction mixture was allowed to stir at room temperature and was then heated to 70°C to initiate the reaction. After 30 minutes of heating, the reaction became exothermic. Once the exotherm had subsided, the mixture was heated to 75°C for four hours. Thereafter, the reaction mixture was cooled to room temperature and filtered resulting in a suspension of solid microspheres.

Then the microsphere suspension was allowed to separate into two phases, the microsphere phase and the decanted phase and was then dispersed in water with 0.8 % by dry weight of a xanthan gum sold under the tradename Kelzan by the Kelco Company. Thereafter, a 48 % by weight water-based dispersion of an acrylate terpolymer containing a N-alkyl substituted acrylamide sold as Hycar 26000X222 by the B.F. Goodrich Company of Akron, Ohio was added at a 4 % concentration by dry weight. Next, ammonium hydroxide was added to increase the pH of the final dispersion from 8 to 10. The final dispersion at 34 % solids was coated at 0.65 grams/square foot at dry weight on a plan recycled bond paper and tested in accordance with the procedures described above. The percentage of the components and the test results are reported in Table 2.

- 23 -

COMPARATIVE EXAMPLE C2

Comparative Example C2 illustrates the use of an adhesive comprising a microsphere adhesive containing no carboxylate groups. No binder was
5 utilized. The microsphere adhesive of this comparative example was prepared in accordance with the procedure outlined in Example 9 except that no acrylic acid was utilized.

COMPARATIVE EXAMPLES C3-5

10 Comparative Examples C3-5 illustrate the use of an adhesive utilizing microspheres with carboxylate groups. No binder was utilized. The microsphere adhesives were prepared in accordance with the procedure outlined in Example 9 except that differing
15 amounts of acrylic acid were utilized. The percentage of the components and the test results are reported in Table 2.

EXAMPLES 11-12

Examples 11-12 also illustrate the use of a
20 water-based acrylamide binder and were prepared in accordance with the procedure outlined in Example 9. The percent Hycar, the peel adhesion and the percent microsphere transfer are reported in Table 2. The percentage of the components and the test results are
25 reported in Table 2.

COMPARATIVE EXAMPLE C6

Comparative Example C6 illustrates the use of an adhesive blend comprising a microsphere adhesive containing no carboxylate groups and Hycar 2600X222.
30 The adhesive blend of this Comparative Example was prepared in accordance with the procedure outlined in Example 9 except that no acrylic acid was utilized. The percentage of the components and the test results are reported in Table 2.

- 24 -

Table 2

Example #	Percent Hycar 2600x222	Micro-sphere IOA/AA ratio	Peel Adhesion (gm/1.25")	Percent Microsphere Transfer
10	4	94/6	100.1	5.2
11	4	98/2	85.3	23.3
12	4	96/4	98.4	8.3
C2	0	100/0	68.0	35.7
C3	0	98/2	79.5	32.1
C4	0	96/4	76.5	19.0
C5	0	94/6	88.9	10.7
C6	4	100/0	83.4	35.2

The test results indicate that microspheres having carboxylated groups have generally less microsphere transfer than those which do not. In addition, the test results indicate that an acrylamide binder reduces microsphere transfer. Indeed, when the composition of the present invention is used, the peel adhesion increases.

EXAMPLES 13-16

Examples 13-16 illustrate the use of a solvent-based acrylamide binder at percent compositions different than those disclosed in Examples 1-12. The adhesive blends of these Examples were prepared in accordance with the procedures outlined in Example 1. The acrylate/acrylamide ratio of the binder, the weight percent of the binder in the dispersion and the test results are reported in Table 3.

- 25 -

TABLE 3

Example #	Binder IOA/ACM Ratio	% by Wt. Binder	Microsphere Transfer (%)
13	92/8	1	11
14	92/8	3	8.7
15	92/8	5	6.5
16	92/8	7	5.0

These test results indicate that an acrylamide binder reduces microsphere transfer when the microsphere is carboxylated.

EXAMPLE 17

Example 17 illustrates the use of an organic dispersion containing hollow microspheres utilizing a carboxylic acid moiety other than that previously described in the examples. The hollow microspheres of this example were prepared in the following manner:

In a one-liter reactor equipped with a mechanical stirrer, condenser and inlet-outlet lines for vacuum and argon, 450 grams of deionized water and 6.0 grams of Standopol-A (Ammonium lauryl sulfate, commercially available from Henkel AG) were charged. The aqueous solution was stirred at 400 rpm, heated to 65° C and degassed with argon. Next, 150 grams of a monomer mixture composed of 144 grams of isooctyl acrylate, 6.0 grams of itaconic acid and 0.71 grams of Lucidol-70 (benzoyl peroxide, commercially available from Pennwalt Corp.) were added to the hot aqueous surfactant solution while stirring at 400 rpm. The temperature was maintained at 65° C for 22 hours. Upon cooling, a suspension of hollow tacky microspheres was obtained.

The binder was prepared in the following manner:

- 26 -

In a glass bottle, 300 grams of ethyl acetate, 0.6 grams of VAZO-64, 16 grams of acrylamide, 0.08 grams of carbon tetrabromide and 184 grams of isooctyl acrylate were combined. The bottle was then
5 purged with argon, sealed and tumbled in a water bath at 55° C for 24 hours. The intrinsic viscosity of the polymer formed was 1.02 dl/gram.

The acrylate/acid ratio of the microsphere, the acrylate/acrylamide ratio of the binder and the
10 test results are reported in Table 5.

EXAMPLES 18-21

Examples 18 to 21 illustrate the use of different acids in microspheres. The microspheres of Examples 18-21 were prepared in accordance with the
15 procedures outlined in Example 17 except that different acids or different amounts of acid were utilized. The alkyl acrylate, the amount of alkyl acrylate, the acid and the amount of acid utilized are reported in Table 4. The acrylate/acid ratio of the microsphere, the
20 acrylate/acrylamide ratio of the binder and the test results are reported in Table 5.

TABLE 4

Example Number	Alkyl Acrylate	Carboxylic Acid
17	144 g. IOA	6.0 g. ITA
18	141 g. IOA	9.0 g. ITA
19	147 g. IOA	3.0 g. FA
20	145.5 g IOA	4.5 g. CRA
21	144.0 g. IOA	6.0 g. AA

- 27 -

TABLE 5

	Acrylate /Acid	Micro- sphere Acrylate /Acid Ratio	Binder Acrylate/ Acryl- amide Ratio	Peel Adhesion (gm/ 1.25)	Micro sphere Trans- fer (%)
17	IOA/ITA	96/4	92/8	28.1	3.9
18	IOA/ITA	94/6	92/8	150.8	0.52
19	IOA/FA	98/2	92/8	155.0	6.9
20	IOA/CRA	97/3	92/8	92.1	19.5
21	IOA/AA	96/4	92/8	92.8	0.16

The test results indicate that compositions of the present invention have reduced microsphere transfer while maintaining sufficient peel adhesion.

COMPARATIVE EXAMPLES C7-11

Comparative Examples C7-11 describe the illustrate the adhesive transfer of microspheres when no binder is utilized. The microspheres were prepared in accordance with the procedure outlined in Example 1. The percentage of the components, the acrylate/acid ratio and the adhesive transfer are reported in Table 6.

TABLE 6

	Acrylate /Acid	Micro- sphere Acrylate /Acid Ratio	Peel Adhesion (gm/ 1.25)	Micro- sphere Trans- fer (%)
C7	IOA/AA	96/4	95.8	5.5
C8	IOA/ITA	96/4	23.7	9.8
C9	IOA/ITA	96/4	112.9	22.1
C10	IOA/FA	98/2	147.3	26.1
C11	IOA/CRA	97/3	70.4	20.0

In summary, novel adhesive compositions has been described. Although specific embodiments and

- 28 -

examples have been disclosed herein, it should be borne in mind that these have been provided by way of explanation and illustration and the present invention is not limited thereby. Certainly, modifications which
5 are within the ordinary skill in the art are considered to lie within the scope of this invention as defined by the following claims including all equivalents.

- 29 -

We Claim:

1. An adhesive composition comprising:
 - a. polymeric, inherently tacky elastomeric microspheres having at least one moiety
5 containing a carboxylic acid group; and
 - b. an adhesive binder comprising at least one acrylamide-based moiety and essentially free of pendant polymeric moiety with a T_g greater than 20°C and a molecular weight in the range of about 2,000 to
10 about 30,000; wherein said microspheres are essentially free of covalent bonding to said binder and said carboxylic acid group and said acrylamide-based moiety are of a type and present in an amount sufficient to substantially prevent microsphere transfer.
- 15 2. The adhesive composition of Claim 1 wherein said binder further comprises at least one acrylic or methacrylic acid ester copolymerized with said acrylamide-based moiety.
- 20 3. The composition of Claim 1 wherein said microspheres further comprise at least one acrylic acid or methacrylic acid ester.
- 25 4. The composition of Claim 1 wherein said microspheres are comprised of at least 85 parts by weight of said acrylic or methacrylic acid ester and up to about 15 parts by weight of said moiety containing a carboxylic group.
- 30 5. The composition of Claim 2 wherein said binder comprises up to about 15 parts by weight acrylamide and from about 85 up to about 100 parts by weight acrylic or methacrylic acid ester.
- 35 6. The composition of claim 1 wherein said binder comprises from about 1 to about 40 parts by weight of said composition and said microspheres comprise from about 60 to about 99 parts by weight of said composition.

- 30 -

7. The composition of Claim 1 wherein said moiety containing a carboxylic group is selected from the group consisting of acrylic acid, fumaric acid, itaconic acid, methacrylic acid and crotonic acid.

5 8. An article comprising a substrate, having applied to at least one surface thereof, a coating of a positionable adhesive composition comprising a blend of:

- 10 a. polymeric, inherently tacky elastomeric microspheres each microsphere having at least one moiety containing a carboxylic acid group; and
- b. an adhesive binder comprising at least one acrylamide-based moiety and essentially free of pendant polymeric moiety with a T_g greater than 20°C and
- 15 a molecular weight in the range of about 2,000 to about 30,000; wherein said microspheres are essentially free of covalent bonding to said binder and said carboxylic acid group and said acrylamide-based moiety are of a type and present in an amount sufficient to
- 20 substantially prevent microsphere transfer.

INTERNATIONAL SEARCH REPORT

Internat'l Application No

PCT/US 94/01872

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C09J133/08 C09J7/02 //(C09J133/08,133:06)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,92 13924 (MINNESOTA MINING & MANUFACTURING COMPANY) 20 August 1992 see claims; examples 1,2 ---	1-8
X	EP,A,0 419 020 (MINNESOTA MINING & MANUFACTURING COMPANY) 27 March 1991 cited in the application see claims; examples 1-3,10-17 ---	1-8
X	EP,A,0 454 365 (MINNESOTA MINING & MANUFACTURING COMPANY) 30 October 1991 see claims; examples 4-7 ---	1-8
A	WO,A,92 11334 (MINNESOTA MINING & MANUFACTURING COMPANY) 9 July 1992 see page 6, line 10 - line 36; examples --- -/--	1



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

27 June 1994

Date of mailing of the international search report

15. 07. 94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

DE LOS ARCOS, E

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 94/01872

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US,A,4 968 562 (JOAQUIN DELGADO) 6 November 1990 see column 7, line 35 - line 42; example 11</p> <p>-----</p>	1